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PURIFICATION OF MINE WATER BY FREEZING

Applied Science Laboratories, Incorporated

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Purification of Mine Water by Freezing

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16. Abstract: Partial freezing of acid mine water was used to the extent of 50% conversion to ice. Various metal and acid components in the product water were consistently in the range of 85 to 90% reduction, with some individual components reduced to 98% on occasion. Acid mine water that had been treated with lime was used in similar freezing experiments and observed to have a reduction of metal ions. The pH remained substantially unchanged and the hardness of the water was reduced by nearly 100%. Considerable variations resulted even with efforts toward good control and reproducibility of operation. A firm conclusion as to reduction of sulfate and reduction of certain individual metals was prevented because of difficulties with analytical results. It is suggested that more reliable data will be obtained if tests are run over a longer pierod of time, on a somewhat larger scale and in the field, so that elimination of irregularities due to collection, transport and storage can take place. (Smith-Texas)

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Purification of Mine Water by Freezing

by

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for the

Department of Mines and Mineral Industries

Commonwealth of Pennsylvania

and the

ENVIRONMENTAL PROTECTION AGENCY

WATER QUALITY OFFICE

Program Number
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February 1971

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ABSTRACT

Acid mine water was subjected to partial freezing to the extent of up to about 50% conversion to ice. It was found that the percent reduction of various metal and acid components in the product water was consistently in the general neighborhood of 85 to 90%, but some individual components were reduced up to 98% in some cases.

Similar percent reduction of metal ions was observed in similar freezing experiments using acid mine water that had been treated with lime. Reduction in hardness of this lime-treated water was found to be nearly 100%, and the pH to remain substantially unchanged.

With reasonable efforts toward good control and reproducibility of operation, there were still considerable variations. Difficulties with analytical results prevent a firm conclusion as to reduction of sulfate, and leave some uncertainty as to individual metals. The limited success of the efforts to overcome this variability indicates that the best way to obtain more reliable data is to run tests (a) over a longer time period, (b) on a somewhat larger scale, (c) in the field, so irregularities due to collection, transport and storage are eliminated.

Office of Saline Water Research and Development Progress Report No. 199, August, 1966 (1) gives plant investment and operating costs for partial freezing of Kittanning Run acid mine water, but these calculations assumed desalinization data were applicable to the acid mine water.

Thus, the next step in a reliable evaluation of partial freezing for purification of acid mine water will require tests and actual operation in the field for a period such as ten days on acid mine waters at different geographic locations.

This report was submitted in fulfillment of Grant 14010 DRZ between the Federal Water Quality Administration and the Commonwealth of Pennsylvania.

Key Words: Acid mine water, freezing purification, ferrous iron reduction, lime-treated acid mine water, hardness reduction, pH change, coal mine drainage.

TABLE OF CONTENTS

Section		Page
	Abstract	i
	Figures	v
	Tables	vii
I	Summary, Including Conclusions and Recommendations	1
II	Introduction	3
	Partial Freezing Purification Methods Earlier Related Work Factors Affecting Success	
III	Source and Handling of Acid Mine Water	7
IV	Analytical Procedures and Calculations	9
V	General Procedure	11
	Variations in General Procedure Bayonet-Type Heat Exchanger - Apparatus Bayonet-Type Heat Exchanger - Procedure	
VI	Results and Discussion	17
	Effect of Storage and of Filtration Prior to Freezing Effect of Rate of Agitation and Rate of Freezing Effect of Rinsing or Washing Extent of Oxidation of Ferrous Iron During Partial Freezing Variation in Successive Layers of Ice	
VII	Tests on Lime-Treated Acid Mine Water	33
VIII	Acknowledgements	37
IX	References and Notes	39
	Appendixes	
	I Other Partial Freezing Experiments	41
	Direct Freezing by Vaporization of "Freon" Indirect Freezing by Vaporization of "Freon" in a Copper Coil Direct Freezing by Addition of Powdered Dry Ice Outdoor Freezing	
	II Analytical Data Arranged by Experiment Number	49
	III Abstracts of Pertinent References	59

FIGURES

No.		Page
1.	Flow Diagram for Partial Freezing of Acid Mine Water	4
2.	Schematic View of the "Bayonet" Type of Heat Exchanger	13
3.	Schematic Top View of the "Bayonet" Type of Heat Exchanger	14
4.	Percent Reduction of Iron Versus Percent Yield of Purified Water	19
5.	Effect of Stirring and Freezing Rate on Percent Reduction of Iron	23
6.	Schematic View of Apparatus for Direct Freezing	43

Preceding page blank

TABLES

No.		Page
I	Condensed Summary of Experiments with Bayonet-Type Heat Exchanger	18
II	Effect of Rate of Stirring and Rate of Freezing	22
III	Scales for the Stir-Freeze Index	24
IV	Effect of Rinsing	26
V	Extent of Oxidation of Ferrous Iron	28
VI	Variation by Layer in Reduction of Impurities in Ice	29
VII	Variation by Layer in Reduction of Impurities in Thin Ice	30
VIII	Effect of Partial Freezing on Lime-Treated Acid Mine Water	34
IX	Direct Freezing by Vaporization of Liquid "Freon"	44

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SECTION I

SUMMARY AND RECOMMENDATIONS

This report describes a series of over 50 batch experiments in each of which a four-liter quantity of acid mine water was subjected to partial freezing to the extent of up to about 50% conversion to ice. After partial freezing, the ice and mother liquor (unfrozen water) were separated. The ice was melted before analysis and these melts are referred to as "product water". It was found that the percent reduction (product water compared with original sample of acid mine water) of various metal and acid components in these waters was in the general neighborhood of 85 to 90%. Individual components were reduced as much as 98% in certain stages of certain experiments. Included in the majority of these water analyses were parts per million total iron, aluminum, manganese, magnesium, calcium, sulfate, and acidity. pH was also determined on most of the samples. In the experiments in which both ferrous iron and total iron were determined, the product water had about the same ratio of ferrous iron to total iron as the original acid mine water, so it appeared there was little oxidation of ferrous iron during the partial freezing experiments.

Similar percent reduction of metal ions was observed in similar freezing experiments using acid mine water that had been treated with lime. With these samples, analyses were made for iron, aluminum, calcium, manganese, magnesium, sulfate, total hardness and pH. Reduction in hardness of this lime-treated water was found to be nearly 100%, but the pH was found to remain substantially unchanged. Difficulties with analytical results prevent a firm conclusion as to reduction of sulfate, and leave some uncertainty as to individual metals.

Partial freezing processes may be carried out in various ways. None of these had been reported as tried on acid mine water prior to the work of this contract. Several such processes were tried in the preliminary experiments of this contract. See Appendix I. Indirect refrigeration with a coolant circulating through a bayonet-type heat exchanger, and with ice formation in solid layers on the heat exchanger surface, was used for most of the experiments because difficulties or disadvantages for laboratory scale testing developed with all other methods.

The 4-liter scale on which the experiments were done is about the largest scale on which laboratory tests can be advantageously conducted, but the nature of the partial freezing process is such that even on this fairly large laboratory scale and with reasonable efforts toward good control and reproducibility of operation, there were still considerable variations in the results. The limited success of the efforts to overcome this variability indicates that the best way to

obtain more reliable data is to run tests (a) over a longer time period, (b) on a somewhat larger scale, (c) in the field, so irregularities due to collection, transport and storage are eliminated.

There is no report prior to that of this contract on experimental tests of partial freezing as a method of purifying acid mine water. Office of Saline Water Research and Development Progress Report No. 199, August, 1966 (1) gives plant investment and operating costs for partial freezing of Kittanning Run acid mine water, but these are calculations only, based on the assumption that the desalinization data are applicable to the acid mine water.

The percent reduction data obtained in the present study and the corresponding percent yields of product water could be applied to the cost estimates of OSW Report No. 199 to obtain somewhat more realistic cost estimates, but these would still be too uncertain to serve as the basis for design of a sizeable pilot plant, or for realistic comparison of partial freezing with other purification methods.

The apparently low yields (up to 50%) of the experiments reported here are not a limitation on practical use. One option is to obtain much greater yields by use of apparatus designed to have greater capacity and thus produce much greater conversion to ice. The data of the present report show that the percent reduction of impurities decreases only slowly as the percent conversion to ice is increased. Extrapolation of these data suggests that apparatus and a procedure that would produce considerably greater conversion to ice would result in ice and product water nearly as pure as has been produced with lower percent conversion to ice and lower yields. A second option is a two-step process. The first ice deposited on the bayonet surfaces (the last ice melted) is always by far the purest, so two "first ices" would increase both the yield and the percent reduction of contaminants. Many variations are possible, and costs might not be greater. Only actual pilot tests of the two-step or multistage process would establish the practical combination of yield and purification, as well as costs.

Thus, the next step in a reliable evaluation of partial freezing for purification of acid mine water will require tests and actual operation in the field for a period such as ten days on acid mine waters at different geographic locations.

The results of the work of this contract definitely show probability of sufficiently good purification and high enough yields to justify such an evaluation program with a multistage testing procedure.

SECTION II

INTRODUCTION

Because of the serious pollution problem caused by the flow of highly acid water from coal mines, the Federal Water Quality Administration and the Commonwealth of Pennsylvania are carrying on an active research and development program on means of purifying such water.

The following report describes work completed under FWQA Grant 14010 DRZ and Commonwealth of Pennsylvania project (CR-88), in which the process of partial freezing was used to reduce the acidity and impurities of acid mine water.

The general state of the art in mine drainage treatment was described by Hill in 1968 (2). His section 9 (pp. 82-85) discusses briefly the possible use of crystallization (freezing) as a method of purification. Hill has also compiled a list of research and development projects of the FWQA in the mine drainage field, beginning 1968 (3). The general concern over this difficult pollution problem has resulted in several symposia under various auspices (4), and in Pennsylvania in the publication of Mine Drainage Abstracts by the Department of Mines and Mineral Industries(5).

Partial Freezing Purification Methods

A partial freezing process has three basic steps, and these are very briefly and simply exemplified here. Figure 1.

Step 1. The mineralized water is refrigerated to convert a considerable fraction of it into ice.

Step 2. As much as possible of the unfrozen water (called mother liquor) is drained off the ice. Almost all the salts remain in the mother liquor.

Step 3. The ice is melted to produce the product water.

The mother liquor can be put through the process again, or may be disposed of in some other manner.

There are numerous ways of constructing and operating a partial freezing plant and some of these have been tested on saline water on a fairly large scale (6). It is not clear as yet which process is best and least costly for saline waters. A process and plant intended for use on mine water would probably be somewhat different from one

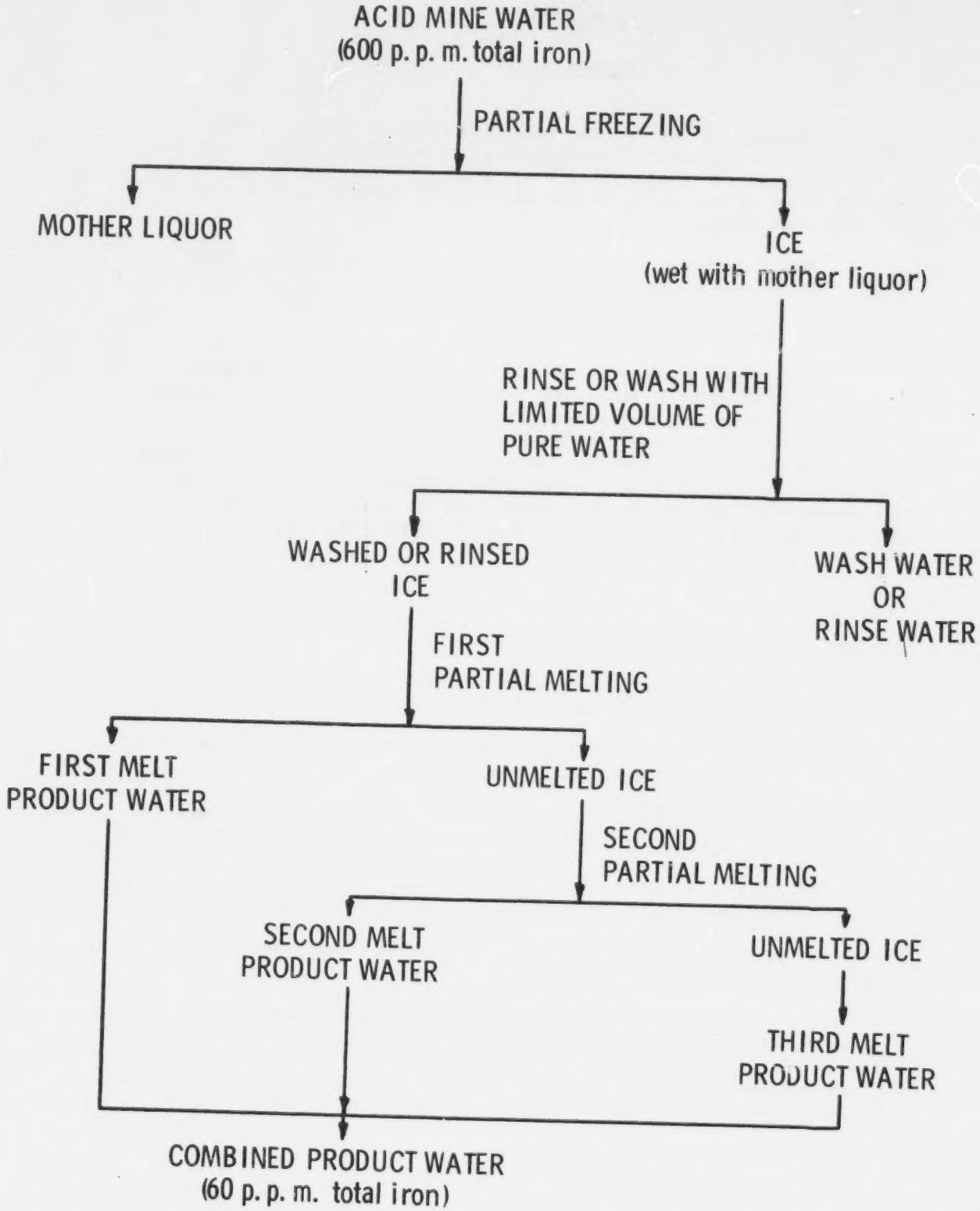

FIG. 1 FLOW DIAGRAM FOR PARTIAL FREEZING OF ACID MINE WATER

designed for salt water or other types of impure water. In general, the development of a practical and economic partial freezing process requires that almost all the impurities remain in the mother liquor and that this mother liquor be small in volume compared to the product water from melted ice.

Most partial freezing processes that have been proposed and tested operate as one step processes (the feed water is subjected only once to partial freezing, and the ice is washed once, and then melted). Processes with two or three steps have been proposed with indications that they may have advantages, but actual tests have been limited.

Earlier Related Work

It appears that there are no published reports of experimental work previous to that of this contract on partial freezing as a means of purification of acid mine water. OSW Research and Development Progress Report No. 199 (1) gives results of calculations of the cost of plant investment and of operating costs for three different types of partial freezing process plants operating on acid mine water from Kittanning Run (near Altoona, Pennsylvania). No actual data on partial freezing of acid mine water were available or used in these calculations. It was assumed that data for desalinization were applicable.

Rose and Sweeny (7) applied partial freezing to the purification of effluent from a conventional secondary municipal sewage treatment plant. Baker and co-workers (8-10) have made extensive studies of partial freezing as a means of concentrating dilute (0.1 to 10 mg/liter) solutions of various metal salts. Their main conclusions were that percent recovery for any given cation did not vary over the concentration range studied, but that larger amounts of initial total dissolved solids decreased percent recovery (caused greater contamination of the product water). As expected, an increase in mixing rate improved percent recovery. The pH also had some effect.

Abstracts of the preceding papers and reports are included in Appendix III of the present report, along with abstracts of a few other papers of peripheral interest (11-12).

Factors Affecting Success

Practical success of the partial freezing process depends on forming a high percent of ice and then melting the ice to a product water substantially free of impurities. Suspended solids or colloidal materials must be removed before partial freezing because they are likely to contaminate the ice by being trapped within it. Some kind of settling, clarification or filtering process is therefore required as a preliminary step.

A critical main step is often the washing process. After partial freezing, the surface of the ice is always covered by a layer of mother liquor, the last of which is sometimes difficult to wash off without using considerable purified product for the washing process. Surface mother liquor not washed off carries its content of dissolved impurities into the melted ice or product water. This occurs with all kinds of impurities.

In general, in partial freezing processes, some of the dissolved impurities always become incorporated within the ice crystals. The tendency for dissolved impurities to become incorporated increases with the concentration of the material dissolved in the solution. This occurs for the following reasons. When a pure ice crystal forms from a solution, the impurities that were dissolved in the water which formed the ice crystal are left behind in the solution surrounding the ice crystal. Consequently, each ice crystal just after the moment of its formation is surrounded by a solution that is more concentrated than the original solution. The next ice growth is thus more likely to be contaminated than previously formed ice.

This increasing tendency toward contamination as more ice forms is somewhat offset by the natural tendency for the dissolved material to diffuse away from the region of increased concentration next to the just-formed ice, and toward the less concentrated parts of the solution from which ice has not yet formed. This offsetting effect may be increased by agitation, or by a decrease in the rate of cooling and freezing, so that there is more time for the diffusion process just mentioned. Sekerka (13) has studied this type of phenomenon in great detail. The main overall conclusions are that vigorous agitation and slow freezing will reduce contamination, but of course, they also tend to increase costs.

When saline waters such as sea water are partially frozen, all or nearly all the salt stays in the mother liquor and substantially no impurities get incorporated within the ice. In general, all dissolved metal salt impurities remain in the mother liquor when any kind of water is partially frozen, but organic impurities vary in their behavior, as do acids. Thus, sewage and other waste water solutions may or may not be successfully purified by partial freezing, and specific tests need to be made to determine the behavior of the impurities when partial freezing is applied.

The main purpose of the work of this contract was to perform such tests on acid mine water to determine the extent to which the impurities went to the mother liquor as compared with incorporation within the growing ice crystals.

A second, but not subsidiary, purpose was to determine the percent reduction of impurities in the product water for various percentage yields of product water from acid mine water.

SECTION III

SOURCE AND HANDLING OF ACID MINE WATER

Two kinds of acid mine water feed were used in these freezing experiments. The primary source was acid mine water issuing from an abandoned well head in the Tyler Run watershed near Hollywood, Pennsylvania (Clearfield County). Twenty to sixty gallon samples were obtained on January 10, February 3, March 19, April 16, May 4 and May 19, 1969. The water was collected in clean dry 5-gallon polyethylene bottles which were almost completely filled before tightly sealing to eliminate effect of air on the water before use in the experiments. The water was kept cool in ice baths until samples were removed for use in actual experiments. Except as otherwise indicated, all such samples of actual acid mine water were passed through a membrane filter just before use in the experiments.

The second source was lime-treated acid mine water obtained from Dr. Harold L. Lovell of the Pennsylvania State University on June 10, 1969. The original source of this water was a well head which was draining Proctor Mine #2 of the New Shawmut Mining Company.

The tables of data show which sample was used in each experiment.

SECTION IV

ANALYTICAL PROCEDURES AND CALCULATIONS

Since the conclusions of this report rest completely on analyses of the acid mine water before and after partial freezing, considerable effort was put into the choice of methods of analysis. Some of these were noted in detail in a preliminary report on this contract (November 14, 1968).

The standard phenanthroline colorimetric method (14) was used for iron in all cases in which both ferrous and total iron were determined, and for total iron in experiments done prior to 809-18.

Atomic absorption spectrometry was used for all other total iron determinations, and for all other metal ions. The method and instrument were those specified by Feige (15). The resonance wave lengths used were the ones recommended by the instrument manufacturer (16).

Sulfate was determined by the barium chloranilate colorimetric method (17).

Acidity was determined by titration with 0.02 N sodium hydroxide solution to the phenolphthalein end point at boiling temperature. Although iron, aluminum and manganese react with some of the sodium hydroxide in this titration, the results are expressed in parts per million of calcium carbonate equivalent to the amount of standard solution titrated (14).

Hardness in the water was determined by EDTA titration (14), also expressed in parts per million calcium carbonate.

Since this titration is not sensitive to lower degrees of hardness, the values around 100 ppm or lower of calcium carbonate equivalent were calculated from ppm magnesium and calcium (14).

pH was determined with a pH meter.

Most of the results of this report are stated in terms of the percent reduction of a single component or of total impurities of the product water or melt as compared with the particular sample of the acid mine water used as starting material. For example, for reduction in total iron content, the following type of calculation was used:

$$\frac{(\text{ml 1st melt} \times \text{ppm Fe 1st melt}) + (\text{ml 2nd melt} \times \text{ppm Fe 2nd melt}) + \ldots}{(\text{ml 1st melt} + \text{2nd melt} + \ldots) \times \text{ppm Fe in starting material}} \times 100$$

$$= x\ \%\ \text{Fe remaining in product water}$$

$$100 - x = \%\ \text{reduction Fe}$$

In order to obtain the percent reduction of total impurities, the percent reduction of each component analyzed was obtained as above, and these then averaged to obtain the percent reduction of total impurities.

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SECTION V

GENERAL PROCEDURE

The general procedure involved the following steps:

1. Collection of acid mine water from its source in the field, transference to State College, and storage with minimum exposure to oxygen, light, and warm temperature.

2. Filtration of acid mine water through a membrane filter just prior to performance of a partial freezing experiment, followed by reservation of a portion of the filtered water for later analysis (see step 6).

3. Cooling of a 4-liter portion of filtered acid mine water until desired percentage conversion to ice was achieved. This was accompanied by measurement of various items of data, as indicated in detail in the Tables.

4. Separation of the ice from the mother liquor, rinsing of the ice in some cases with separate collection of the rinse, and transfer of the ice to a clean vessel where it was allowed to melt. Usually the product water was obtained in several melts.

5. The volume of each of the melted ice fractions was measured and one or more samples then analyzed and otherwise tested. The mother liquor, the rinse (if any) and the original acid mine water reserved in step 2 were also measured and analyzed.

Variations in General Procedure

Step 3 of the preceding section, i.e. the actual cooling to achieve partial freezing, was carried out in a number of ways, as indicated in the following paragraphs, in the order in which they were tried.

1. Natural outdoor freezing with minimal agitation.

2. Controlled addition of powdered dry ice directly into the acid mine water.

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3. Controlled release of compressed liquid "Freon 12" directly into the acid mine water whereupon the vaporization of the "Freon" absorbs heat and causes cooling and partial freezing.

4. Indirect or secondary cooling of the agitated acid mine water by a copper cooling coil through which cold liquid "Freon 12" is circulated from a conventional refrigerating unit.

5. Indirect or secondary cooling of the agitated acid mine water by a bayonet-type heat exchanger through which a cold liquid coolant (mixture of water and ethylene glycol) is circulated from a conventional refrigerating unit.

Method 1 (direct outdoor freezing) was tried to determine whether there was a possibility of developing a relatively crude but probably inexpensive method for use during cold weather.

Method 2 (dry ice addition) was tested to observe the effect of very rapid freezing.

Methods 3 and 4 could not be operated successfully. Method 3 would have been preferred since all partial freezing desalting processes that have been tested use direct freezing in which a compressed liquid refrigerant is released and expanded directly into the water to be purified. In some cases, water itself is vaporized to produce the refrigeration. This method was not used further in this contract because the ice (probably a "Freon" hydrate) was produced in such a form that it could not be handled or separated from the mother liquor in a satisfactory manner. These first four methods are described in Appendix I.

Method 5 (indirect freezing with the bayonet-type heat exchanger) proved to be relatively simple to operate. It was preferable to method 4 (copper coil heat exchanger) because the bayonet exchanger provided a greater surface area in contact with the water being cooled and so permitted more rapid cooling. This method was used for most of the experiments of this contract and the results are therefore presented first in the report and are the basis for the general conclusions expressed.

Bayonet-Type Heat Exchanger - Apparatus

The general nature of the apparatus is indicated in Figures 2-3. A five-liter glass jar, 12 inches in height, 6 inches in diameter, served as the receptacle for the acid mine water and the bayonet exchanger. The latter can best be visualized from Figure 2. At the top is a copper box 4 5/8 inches wide, 5 1/8 inches long, and 2 3/8 inches high. It is divided into an inlet and an outlet chamber, with corresponding inlet and outlet tubes. These are 3/8 inch O.D. and 5/16 inch I.D.

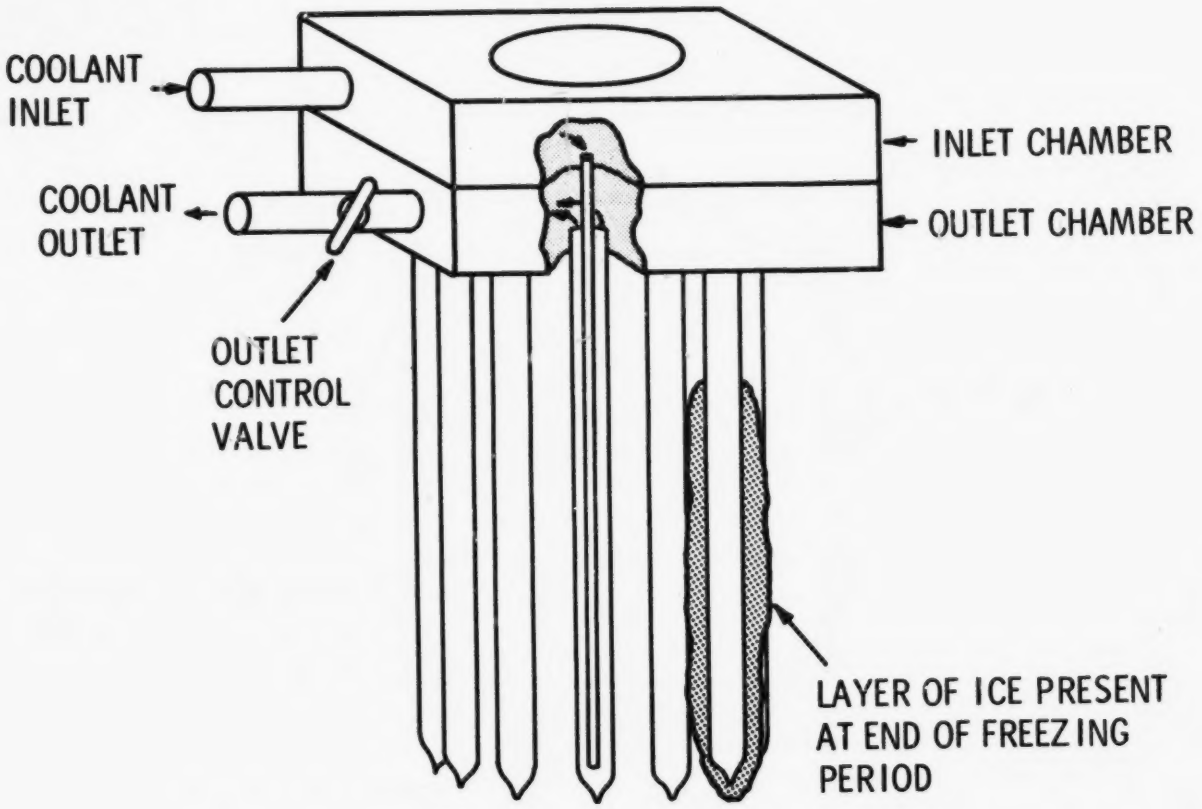

FIG. 2 SIDE VIEW OF THE "BAYONET" TYPE OF HEAT EXCHANGER

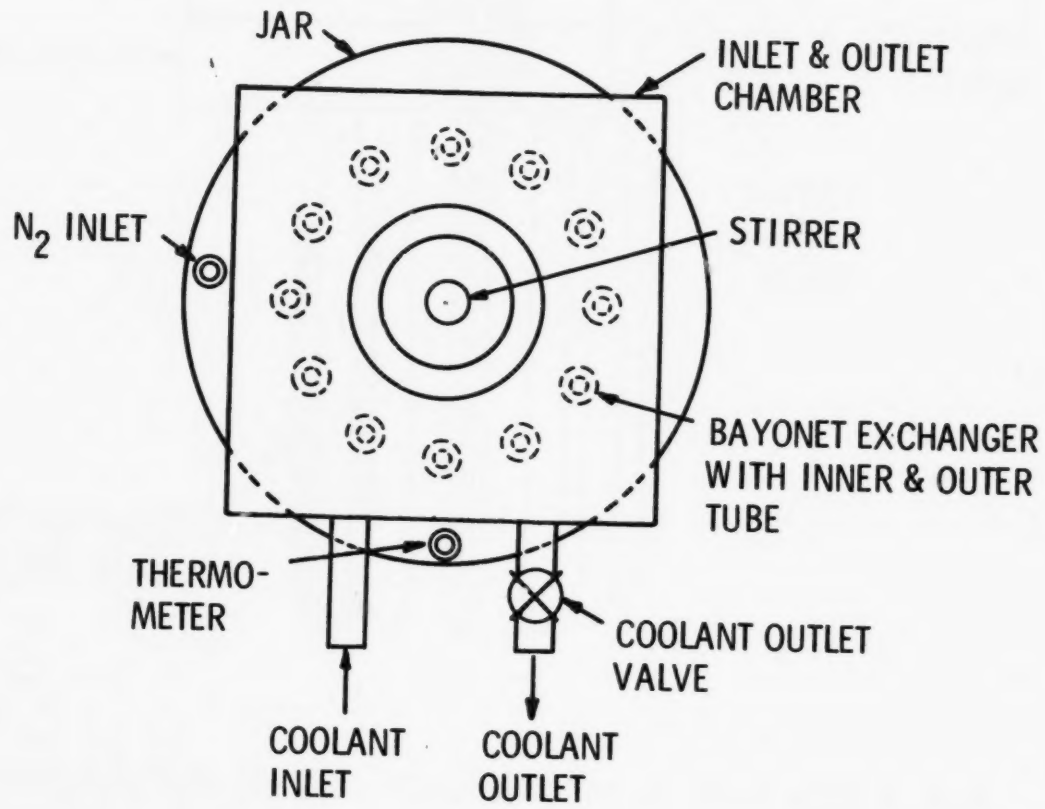

FIG. 3 SCHEMATIC TOP VIEW OF THE "BAYONET" TYPE HEAT EXCHANGER

The twenty bayonets are 12 1/8 inches long, and are hollow. An inner tube 1/8 inch O.D. extends into the inlet chamber, and the surrounding outer tube, 1/4 inch O.D., extends only into the lower outlet chamber. There is thus a circulation of coolant from the upper inlet chamber down through the inner tube of the bayonet into the outer tube and up to the lower chamber of the copper box, and back to the refrigerating unit.

The total surface area of the bayonets is 911 sq. cm., and the ratio of the volume of acid mine water to this surface is 4.4 ml per sq. cm.

Bayonet-Type Heat Exchanger - Procedure

At the start of an experiment, a four-liter quantity of acid mine water was prepared by filtration of a somewhat larger quantity of the original acid mine water. A small portion of the filtered water was set aside for analysis. Four liters of the filtered acid mine water was poured into the freezing jar and the bayonet-type heat exchanger placed in position. The refrigerant flow was started through the exchanger and the stirring action begun. The temperature and flow rate of the coolant, and the degree of agitation were varied in different experiments to obtain different freezing rates and thus different percentage conversions to ice in the separate experiments. The temperature of the coolant was measured in the coolant inlet line just before the coolant entered the bayonet heat exchanger.

In all experiments subsequent to 809-11 (except 809-16), a small amount of powdered ice was added to the acid mine water toward the end of the cooling period when the water temperature had reached +0.2°C. When this was done, clear ice began to form on the heat exchanger surface as soon as the acid mine water temperature reached 0°C. Clear ice continued to form as the experiment progressed and there was no evidence of supercooling of the acid mine water.

The degree of agitation was varied by controlling power input to a mechanical stirrer by use of a Variac transformer. In earlier experiments, the stirrer was a single blade type, and in later experiments, an auger type. In many experiments, a stream of nitrogen was bubbled through the acid mine water to provide an additional stirring effect and also to reduce the rate of oxidation of the ferrous iron. After some trials of slow and moderate rates of stirring, it appeared that the most rapid rate of stirring that was possible with the equipment would give the greatest percent reduction of impurities and in all subsequent experiments, fast stirring was adopted as the regular standard procedure. This result is not surprising because it is in accord with the general principles of the diffusion, mixing and crystallization that are occurring at the point of ice formation and determining the percent reduction in impurities.

Several kinds of data were recorded as the layer of ice formed and thickened on the outside surface of the fingers of the heat exchanger. When it was judged that the desired quantity of ice had formed, refrigerant flow was stopped. The exchanger was disconnected and transferred with its ice coating to a clean jar where it was rinsed, if rinsing was to be included in the experimental test.

The exchanger was then transferred to another clean jar where melting was allowed to occur. In most cases, still further transfers to clean jars were made to collect melt in several portions. Melt I would then represent the outer layer of ice, melt III (usually) the inner layer or first ice formed, and melt II the intermediate layer. Samples of the original filtered acid mine water, the mother liquor, the rinse liquid, if any, and the several melts were reserved for analysis after measuring the quantity of each of these liquids.

The key items of the preceding description of the procedure may be recapitulated by listing the several variables or factors that influenced the procedure or the results.

1. Period of storage of water between obtaining sample and doing the experiment.
2. Filtration with the bacterial filter.
3. Rate of freezing.
   a. Temperature of coolant
   b. Flow rate of coolant
4. Duration of cooling period.
5. Use of nitrogen stream for agitation, and to restrict oxidation.
6. Type of mechanical agitator and rate of agitation.
7. Seeding with powdered ice.
8. Use of rinse water.

SECTION VI

RESULTS AND DISCUSSION

The important items of the results were:

1. Percentage of acid mine water converted to ice and product water.
2. Percent reduction of iron and other impurities of the acid mine water.
3. Effect of rate of agitation and rate of freezing.
4. Effect of storage and of filtration prior to freezing.
5. Effect of seeding with ice.
6. Effect of rinsing.
7. Extent of oxidation of ferrous iron.
8. Variation in successive layers of ice.

Analytical data for all the experiments are given in detail in Appendix II. Table I gives a condensed summary of the conditions and results of all the bayonet-type heat exchanger experiments. Probably the most interesting figures cited in that table are on line 5 (percent conversion to ice) and lines 8 to 12 (showing percent reduction of certain components, of total components, and the change in the pH). A partial summary of these is given in Figure 4, which shows that the percent reduction of iron can be over 90% regardless of whether the conversion to ice is as low as 10% or over 40%. Some of the individual layers of ice (melts) showed up to 98% reduction of certain impurities.

The erratic nature of the data arises mainly from the fact that acid mine water and all the samples obtained from it in the partial freezing process are a mixture of a very dilute solution and a very finely divided dispersed solid made up of iron and other hydroxides and related basic salts. The presence of even a very small amount of the dispersed solid causes a relatively large change in the overall composition of the solution in which the solid is dispersed. Attempts to eliminate this variability are discussed in a following section on Effect of Storage and of Filtration Prior to Freezing.

TABLE I

CONDENSED SUMMARY OF EXPERIMENTS WITH BAYONET-TYPE HEAT EXCHANGER

Number of Experiment*	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	27	29	32	34	38	40	43	44	47	49	50	53	54	55	57	58	59	60	61
Date Water Obtained (1969)	2/3	2/3	2/3	2/3	2/3	2/3	2/3	3/19	3/19	3/19	3/26	3/26	4/1	4/1	3/19	3/19	3/19	4/16	4/16	4/16	4/16	4/16	4/16	5/4	5/4	5/4	5/4	5/4	5/4	5/19	5/19	5/19	5/19	5/19
Date Experiment Done (1969)	3/5	3/6	3/6	3/7	3/7	3/10	3/10	3/19	3/19	3/20	3/26	3/28	4/1	4/2	4/7	4/9	4/10	4/17	4/18	4/21	4/22	4/24	4/25	5/5	5/6	5/7	5/12	5/13	5/15	5/20	5/21	5/22	5/22	5/23
Days Until Experiment Done	30	31	31	32	32	35	35	<1	<1	1	(g)	(g)	(h)	(h)	19	21	22	1	2	5	6	8	9	1	2	3	8	9	11	1	2	3	3	4
% Conversion to Ice (a)	51	11	11	15	47	12	12	21	19	53	20	39	34	31	31	32	37	23	21	23	39	41	34	28	35	12	42	43	31	24	42	13	9	9
Total Iron in Acid Mine Water, ppm (b)	400	400	880	880	880	1080	1020	600	720	760	--	--	940	872	856	816	784	692	216	656	424	640	576	640	608	680	548	568	540	580	556	568	552	568
Total Iron in Mother Liquor, ppm	390	621	975	945	800	1035	1205	800	800	1080	--	--	1300	1288	1024	1040	1032	936	172	800	496	824	668	784	840	640	800	832	736	688	880	620	608	608
% Reduction - Total Fe Only (c)	--	27	61	54	19	30	66	50	39	28	--	--	58	75	55	66	53	84	65	69	42	60	39	93	90	94	86	88	87	92	91	93	93	93
% Reduction - SO_4 Only (c)	--	--	--	--	--	--	--	21	61	44	6	61	64	42	--	--	--	89	62	77	31	53	38	91	89	94	89	90	88	92	90	93	97	92
% Reduction - Acidity Only (c)	--	30	64	57	35	18	67	--	--	--	--	--	--	--	61	74	62	84	89	74	50	66	38	92	90	92	85	88	85	92	89	93	94	92
% Reduction - All Components (d)	--	28	63	56	27	24	66	42	38	33	6	61	61	58	56	73	54	88	81	74	39	54	31	85	85	89	84	86	84	90	87	91	91	91
pH Last Portion of Ice to Melt / pH Acid Mine Water Used	--	--	--	--	--	--	--	4.5 / 4	4.5 / 3.5	5 / 4	6 / 4.5	6 / 4.5	5 / 2.5	5 / 3	5 / 4	5 / 4	5 / 4	5.5 / 4	5 / 4	5.5 / 3.5	4.5 / 4	3.7 / 2.9	2.5 / -	4.3 / 3.2	4.1 / 3.3	4.3 / 3.5	4.4 / 3.1	3.7 / 3	3.7 / 3.1	4.4 / 3.3	4.3 / 3.4	4.4 / 3.4	4.1 / 3.3	4.1 / 3.6
Extent of Analysis	← Total Fe and Acidity →							← Total Fe, Al, Mn, Mg, Ca, SO_4 →			← SO_4 Only →		← Total Fe, SO_4 →		← Total Fe, Al, Mn Mg, Ca, Acidity →			← Total Fe, Al, Mn, Mg, Ca, SO_4, Acidity →															
Ferrous Iron Analysis, +	--	--	--	--	--	--	--	--	--	--	--	--	+	+	+	+	+	+	--	+	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Filtered (F) or Not Filtered (U)	U	U	U	U	U	U	U	U	U	U	U	U	U	U	F	F	F	F	U	U	F	F	F	F	F	F	F	U	F	F	F	F	F	F
Rinse Used, +	--	--	--	--	--	--	+	+	+	+	+	+	+	+	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Nitrogen Bubbling to Stir, +	--	--	--	--	--	--	--	--	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Auger Stirrer with Turbine Blade, + (S Indicates Mechanical Stirrer with Double Blade; 0 Indicates No Mechanical Stirrer)	S	S	S	S	S	S	S	+	0	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Variac Setting of Stirrer (F Indicates Mechanical Stirrer Operated at Fast Speed)	F	F	F	F	F	F	F	F	0	F	40	40	50	70	70	70	57	60	70	70	40	25	25	70	70	70	70	70	70	70	70	70	70	70
Stirring Rate Index (f)	--	--	--	--	--	--	--	--	--	--	1	1	1.5	2	2	2	1.5	1.5	2	2	1	0	0	2	2	2	2	2	2	2	2	2	2	2
Temperature of Coolant, °C	--	-15	-15	-15	-15	1	-15	-10	-12	-9	-15	-8	-15	-15	-17	-13	-16	-9	-9	-14	-17	-6	-16	-8	-8	-8	-8	-8	-8	-8	-8	-8	-8	-8
Duration of Cooling, Minutes	--	15	20	20	71	1	138	24	22	116	50	75	60	50	30	49	45	60	79	30	40	98	33	100	120	60	125	120	110	116	120	32	30	32
Freezing Rate, ml/minutes	--	29	22	30	27	1	36	35	34	18	16	21	23	25	40	26	33	15	10	30	39	17	41	11	11	8	14	14	11	9	14	16	12	12
Freezing Rate Index (f)	--	0	.5	0	.5	1	1	.5	.5	1.5	1	1.5	.5	.5	0	1	0	2	2	0	0	2	0	2	2	2	2	2	2	2	2	2	2	2
Stir-Freeze Index (f)	--	--	--	--	--	--	--	--	--	--	2	2.5	2	2.5	2	3	1.5	3.5	4	2	1	2	0	4	4	4	4	4	4	4	4	4	4	4

Footnotes and Remarks

*All experiment numbers should be preceded by 809-.

(a) Same as % conversion to product water, and includes water from first, second and any additional melts.

(b) Variations for water obtained on same date are due to oxidation, precipitation and other changes during storage or experimentation.

(c) The percentage given is for the content in the total of the melted ice as compared with the acid mine water used as starting material. See text under Analytical Procedures and Calculations.

(d) Percentage given is simple average for % reduction of all components listed under "Extent of Analysis".

(e) In all experiments in which ferrous iron was determined, the same method (phenanthroline colorimetric method) was used for total iron. This method was also used for total iron in experiments 11 to 17.

(f) See Table III and text under Effect of Rate of Agitation and Rate of Freezing.

(g) Synthetic solution of sodium sulfate and hydrochloric acid. No iron present.

(h) Synthetic solution of ferrous ammonium sulfate.

(i) Experiment 16 was done without seeding and with very rapid cooling. Supercooling and flash freezing occurred.

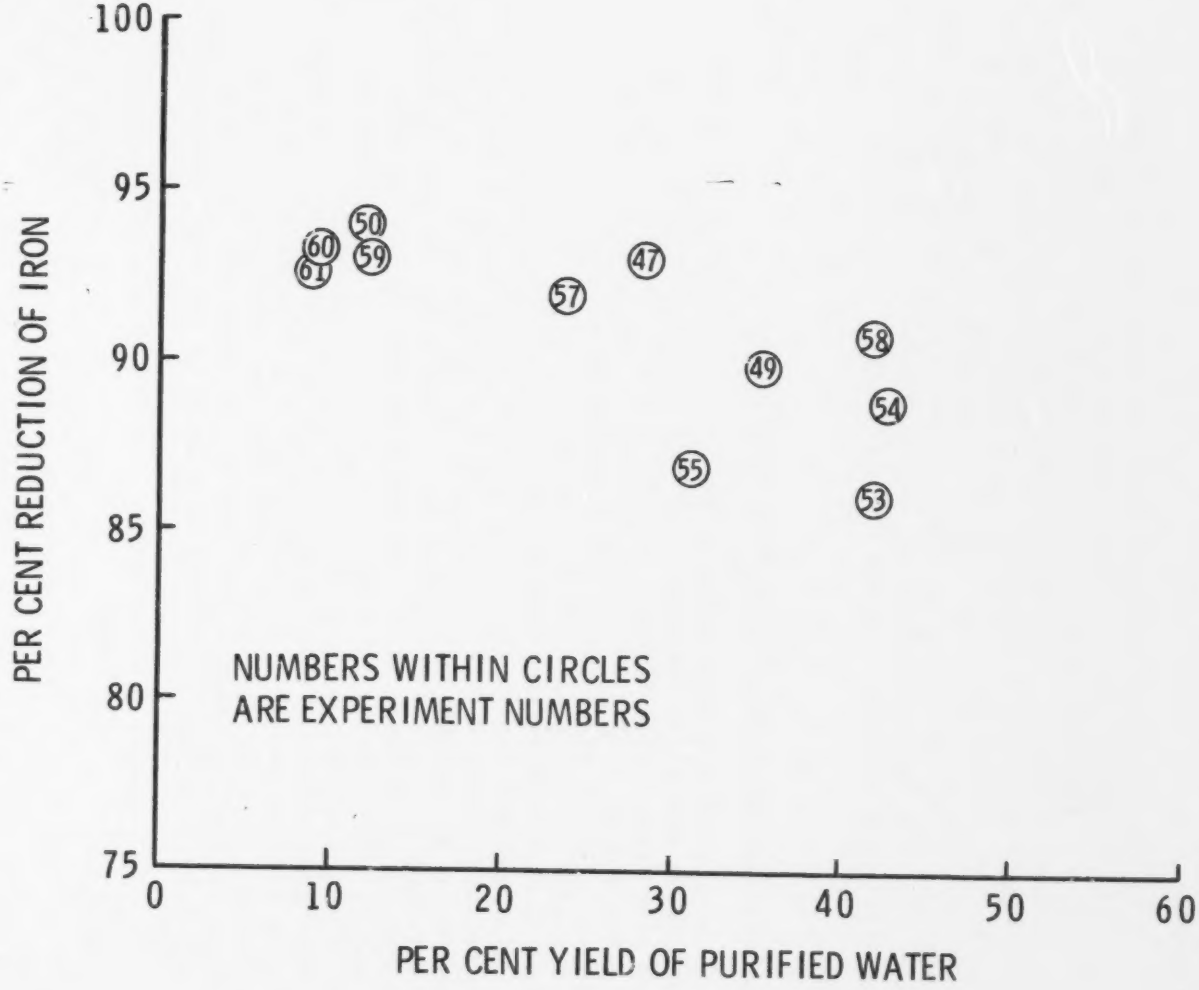

FIG. 4 - PERCENT REDUCTION OF IRON VERSUS PERCENT YIELD OF PURIFIED WATER

The apparatus used for these experiments limited the percent conversion to ice to a maximum of 50%. The heat being removed to cause freezing had to pass through a gradually thickening layer of ice as the experiment proceeded. The apparatus used had no means for removing part or all of this layer of ice during the freezing period of an experiment. The increased amount of ice also tended to reduce the effectiveness of agitation and the transfer of heat through the film at the interface where ice was forming. Consequently, the rate of removal of heat from the unfrozen water gradually decreased during an experiment until the rate of formation of ice became so slow that it was impractical to continue the experiment even though the coolant temperature, flow rate, and the rate of agitation were adjusted to the maximum extent.

It is possible that with different apparatus that would permit higher percent conversions to ice, this procedure would still achieve up to or over 90% reduction of the content of impurities. This is important because a sufficiently high percentage conversion to ice with a single freezing operation would result in a simpler and less costly process, as well as a smaller volume of the mother liquor containing the impurities and a simpler method for its ultimate disposal. Laboratory scale experiments are not likely to give conclusive data in this connection because of the inherent variability of acid mine water, so that field tests on sizeable quantities of water will probably be necessary.

Effect of Storage and of Filtration Prior to Freezing

As stated in the preceding section, appreciable variations of different kinds were noted throughout the work because of changes in the acid mine water during storage, apparently due to oxidation of the ferrous iron and the hydrogen sulfide, as well as other changes. These resulted in formation of colloidal and suspended materials, the latter of which tended to settle out. These changes occurred with appreciable rapidity, so that even at temperatures below 50°F (10°C), appreciable yellow color and some brown precipitate appeared after a 12-hour overnight storage period. The most serious effect of the dispersed solid arises because some of it becomes entrapped within the ice during the ice formation, and thus reduces the percentage reduction of impurities. A more obvious, but less important behavior of the dispersed material is its tendency to collect at the water-ice interface and thus increase the impurities content of the outermost layer of ice. In certain experiments, this effect was large enough to cause the impurities content of the outermost layer to be greater than that of the original acid mine water or the mother liquor. This is especially likely when the first melt is small in volume. In some experiments, the quantity of first melt water was small enough to correspond to melting of a layer of ice only about 0.1 mm in thickness.

Filtration of acid mine water just before an experiment was started decreased the proportion of dispersed solid in the water, but did not eliminate this material. It was noted that after filtration, the acid mine water was still slightly yellow in color. Lowering of the temperature prior to freezing causes lower solubility and precipitation of additional solid material. Filtration at a temperature just above the freezing point was considered, but not used because of the complexity of the apparatus and procedure, because filtration would not completely remove the solid anyway, and because it appeared that the erratic nature of the data was not extensive enough to seriously interfere with its interpretation for the purposes of the present study.

The changes in suspended and colloidal material continued to occur throughout the period of storage, so that in general, each experiment was done on what amounted to a different acid mine water.

Although the oxidation proceeds spontaneously in the presence of air, it is widely believed that certain bacteria markedly hasten this reaction (19). Hence, in most of the later experiments, the samples were filtered through a bacterial filter just before an experiment was commenced (20). Even after this filtration, the water retained a slight yellow brown color indicative of colloidal iron material in suspension. The variability of the results was decreased, but by no means eliminated, by the use of the bacterial filter.

The best way to completely eliminate the dispersed material would be to carry out the partial freezing in the field under circumstances where the acid mine water could be transferred directly into the processing plant from the formation where it occurred underground or from the point where it issues into the atmosphere. This would eliminate the effect of oxygen in causing the formation of insoluble material. Cooling and freezing by direct vaporization of a liquid hydrocarbon such as butane or isobutane, as is common in water desalting plants that operate with partial freezing, would further restrict the possibility of the formation of suspended impurities.

Further investigation of partial freezing methods for purification of acid mine water should take the phenomenon of the preceding paragraphs into consideration.

Effect of Rate of Agitation and Rate of Freezing

Table II and Figure 5 indicate that a slow rate of freezing accompanied by vigorous agitation gives the best percentage reduction of the impurities in acid mine water. The effectiveness rating is based upon an arbitrary combination of rough (and also arbitrary) overall scales expressing the degree of agitation and the rate of cooling in the different experiments. These are shown in detail in Table III. The maximum value

TABLE II

Effect of Rate of Stirring and Rate of Freezing

See Table III for Explanation of Index Scales Used

Exp. # 809-	Variac Setting of Stirrer/ Stirring Rate Index	Coolant Temp. °C/ Freezing Rate Index	Freezing Rate ml/min/ Freezing Rate Index	Stir-Freeze Index	% Reduction Fe
25	70/2	-17/0	40/0	2	55
27	70/2	-13/0.5	26/0.5	3	66
29	57/1.5	-16/0	33/0	1.5	53
32	60/1.5	- 9/1	15/1	3.5	84
34	70/2	- 9/1	10/1	4	65
38	70/2	-14/0	30/0	2	69
40	40/1	-17/0	39/0	1	42
43	25/0	- 6/1	17/1	2	60
44	25/0	-16/0	41/0	0	39
47	70/2	- 8/1	11/1	4	93
49	70/2	- 8/1	11/1	4	90
50	70/2	- 8/1	8/1	4	94
53	70/2	- 8/1	14/1	4	86
54	70/2	- 8/1	14/1	4	88
55	70/2	- 8/1	11/1	4	87
57	70/2	- 8/1	9/1	4	92
58	70/2	- 8/1	14/1	4	91
59	70/2	- 8/1	16/1	4	93
60	70/2	- 8/1	12/1	4	93
61	70/2	- 8/1	12/1	4	93

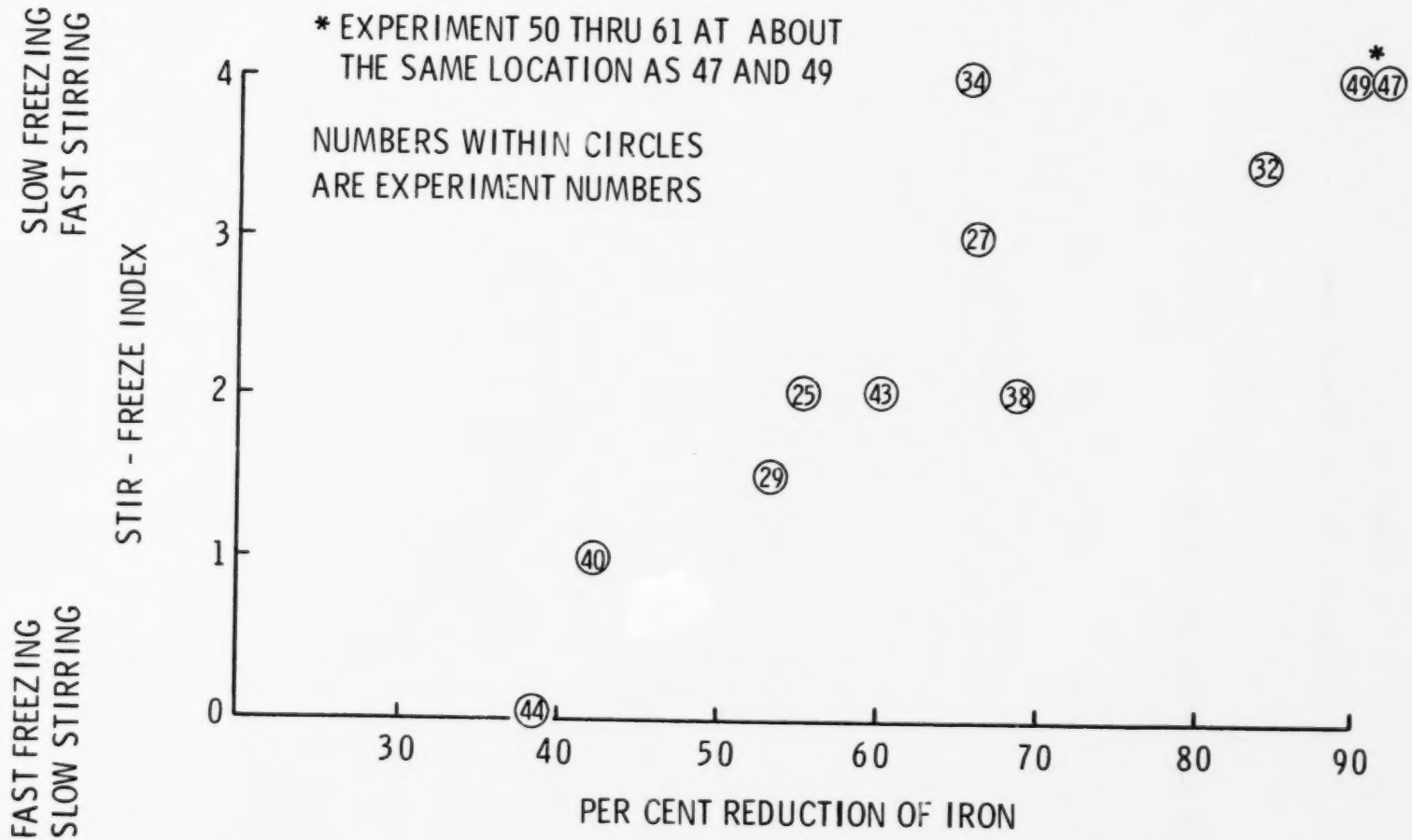

FIG. 5 - EFFECT OF STIRRING AND FREEZING RATE ON PERCENT REDUCTION OF IRON

TABLE III

Scales for the Stir-Freeze Index

A. Stirring Rate Index Contribution

Variac Setting	20	28	36	48	68	70
	Slow Stirring		Medium Stirring		Vigorous Stirring	
Contribution to Index	0	1/2	1	1-1/2	2.0	

B. Freezing Rate Index Contribution

1. Effect of Coolant Temperature

Coolant Temperature °C	-6 -8 -9	-10 -12 -13	-14 -16 -18
	Slow Freezing	Medium	Fast Freezing
Contribution to Index	1	1/2	0

2. Effect of Freezing Rate

Freezing Rate in ml/min	5 10 15	20 25	30 35 40 45
	Slow Freezing	Medium	Fast Freezing
Contribution to Index	1	1/2	0

Stirring rate index (A) plus freezing rate index (B1 and B2) equals stir-freeze index.

of 4 on this overall rating scale (the stir-freeze index) corresponds to a rating level of 2 (stirring rate index) for vigorous agitation with a setting of 70 on the Variac transformer providing power to the agitator, plus an additional rating level of 2 (freezing rate index) for slow cooling due to a combination of a coolant temperature in the range -6 to -10°C and a consistent low freezing rate in the range of 8 to 10 ml per minute. An overall rating of 0 on the scale would result from a Variac setting of 25 for agitator power, with a coolant temperature in the range of -14 to -17°C and a freezing rate of 30 or more ml per minute. (Note Experiment 44 on Fig. 5.) Intermediate overall ratings of 1, 2 or 3 correspond to various combinations of intermediate power settings for the agitator with intermediate coolant temperatures and freezing rates.

Figure 5 shows points corresponding to the percent reduction of total iron and the overall agitator-cooling rating for experiments 809-25, 27, 29, 32, 34, 38, 40, 43, 44, 47 and 49. The points for experiments 809-50 through 61 are not shown because they would all fall in the same area of the graph as 809-47 and 49.

It is not surprising to find that vigorous agitation and a slow rate of freezing give the best percentage reduction of impurities, as explained in the Introduction under Factors Affecting Success.

Effect of Rinsing or Washing

Since the bayonet cooler produced the ice as solid blocks or layers on the heat exchanger, there was relatively little ice surface on which mother liquor could collect. In consequence, it would be expected that rinsing would have little effect. Rinsing was used in a few of the early experiments and then not used further because no beneficial effects were observed. It appeared that other factors completely overshadowed any effect of rinsing. This is shown in Table IV which gives percentage reduction information for several experiments in which rinsing was used, along with other experiments done at about the same time, but without rinsing.

Extent of Oxidation of Ferrous Iron During Partial Freezing

In a number of experiments, both ferrous iron and total iron were determined in the starting material (acid mine water), and in the several fractions resulting from the experiment. Similar experiments were done with synthetic solutions containing only ferrous ammonium sulfate with iron in about the concentration present in the acid mine water. These experiments were done by the standard indirect freezing procedure with the bayonet heat exchanger for cooling, using a four-liter quantity of starting material, and seeding with powdered ice at +0.2°C. The

TABLE IV

Effect of Rinsing

Exp. # 809-	% Reduction Total Fe	% Reduction Total Fe in Outside Ice Layer re Mother Liquor
With Rinsing		
17	66	71
18	50	20
19	39	45
23(a)	58	18
24(a)	75	57
Without Rinsing		
25	55	11
27	66	31
29	53	7

(a) Synthetic solution of ferrous ammonium sulfate.

results of these experiments are summarized in Table V, which gives the ratio of ferrous iron to total iron in the several fractions from each of a series of experiments.

It was found that the ratio of ferrous iron to total iron was slightly less in the product water than in the starting material and mother liquor. The average for the first and second melts showed only a slightly decreased ratio (0.90 to 0.88 and 0.87). The third melt showed a decrease from 0.90 to 0.75. This suggests that there was very little oxidation of ferrous iron during the actual freezing part of the experiments, but that oxidation during and after melting was more rapid.

The considerable variability in the individual results is probably due to the presence of varying quantities of suspended iron hydroxide or basic salts or similar materials. These materials are erratically distributed during all parts of the overall procedure.

If a hydrocarbon gas were used as a direct refrigerant, as is the case in most partial freezing processes for water desalting, there could be only slight oxidation because the water and ice would be covered by a blanket of gaseous hydrocarbon.

Variation in Successive Layers of Ice

In almost all of the experiments, the ice was melted in three separate steps to produce a first, second, and third melt. The first melt was formed from the outermost portion of ice, i.e., the last ice to form during the freezing period. The third melt was formed from the innermost portion of ice, i.e., the first ice to form during the freezing period. The second melt was then an intermediate layer of ice formed at an intermediate time during the freezing period.

Table VI shows a comparison of the percent reduction of impurities for several melts or layers of several experiments. All experiments were done with vigorous stirring and a slow rate of freezing. Averages for the three layers of experiments 47, 49, and 55, and their total ice layers may be examined, as well as averages for the innermost layer of experiments 53, 54, and 58. The last line gives averages for the total ice of experiments 50, 59, 60, and 61, chosen because even the total ice was quite thin. This last set of values is further broken down in Table VII into layers.

The results are strikingly consistent. The innermost layers always show the best percent reduction of impurities. The outermost layers always show the poorest percent reduction, and the intermediate layers show intermediate reduction.

TABLE V

Extent of Oxidation of Ferrous Iron

Experiment Number	23(a)	24(a)	25	27	29	32	38	Average
Ratio Ferrous Iron/ Total Iron								
Starting Material	0.97	0.96	0.85	0.86	0.93	0.93	0.81	0.90
Mother Liquor	0.95	0.98	0.93	0.93	0.93	0.86	0.83	0.91
First Melt	0.93	1.00	0.91	0.88	0.89	0.76	0.81	0.88
Second Melt	0.96	0.94	0.94	0.59	0.85	1.00	0.83	0.87
Third Melt	0.67	0.75	0.81	0.75	0.72	0.89	0.67	0.75
Percent Reduction								
All Components	61	58	56	73	54	88	74	
Total Iron Only	58	75	55	66	53	84	69	
Sulfate Only	64	42	--	--	--	89	77	
pH Change (b)	2.5/5	3/5	4/5	4/5	4/5	4/5.5	3.5/5.5	
Percent Conversion to Ice	34	31	34	31	37	23	23	

(a) Experiments 23 and 24 based on synthetic solutions of ferrous ammonium sulfate.
(b) Represents pH of starting material over pH of last portion of ice to melt.

TABLE VI

Variation by Layer in Reduction of Impurities in Ice

Experiment Numbers 809-	Position of Ice Layer	Average % Conversion to Ice	Average % Reduction of Impurities	Range of % Reduction of Individual Impurities	Stir-Freeze Index
47, 49, 55	all layers	31	85	70-93	4
	outer layer	3	42	0-59	4
	intermediate layer	5	79	54-87	4
	innermost layer	24	93	86-97	4
53, 54, 58	innermost layer	28	94	88-98	4
50, 59, 60, 61 (see also Table VII)	thin ice layer	11	91	83-97	4

TABLE VII

Variation by Layer in Reduction of Impurities in Thin Ice

Experiment Numbers 809-	Position of Ice Layer	% Conversion to Ice	% Reduction of All Impurities	% Reduction Individual Impurities						
				Fe	Al	Mn	Mg	Ca	SO_4	Acidity
59	total all layers	13	91	93	93	87	90	87	93	93
	outside layer	2	73	77	75	78	71	63	70	78
	innermost layer	11	94	96	96	90	94	92	97	95
60	total all layers	9	91	93	92	87	90	84	97	94
	outside layer	1	66	69	67	67	65	43	78	71
	intermediate layer	1	86	88	82	89	84	74	96	88
	innermost layer	7	94	97	97	89	94	90	96	97
61	total all layers	9	91	93	92	87	92	87	92	92
	outside layer	1.5	74	77	77	78	72	63	74	78
	innermost layer	7.5	95	97	96	89	96	92	97	96

The increase in the concentration of impurities in proceeding from the inner to the intermediate and outer layers of ice is certainly related to the gradual increase that takes place in the concentration of impurities in the unfrozen mother liquor as a freezing experiment progresses. The magnitude of the differences in concentration of impurities from one layer to the next is surprisingly large, so that other phenomena may be occurring.

Even more surprising is the indication from the results in Table VII that the effect is independent of the percent conversion to ice. Thus, Table VII shows the same progressions of percent reduction from innermost to outermost ice layers in experiments with 9 to 13% conversion to ice, as existed in experiments with 24% or greater. Table VI shows that the percentage reduction of the innermost layer of the earlier experiments (with over 24% conversion to ice) is a little greater than the percentage reduction for the entire quantities of ice in the experiments with only 9 to 13% conversion to ice.

These results suggest that there may be some appreciable diffusion of impurities through the innermost layers of ice during the latter part of the freezing period and in the melting period. A phenomenon of this general nature has been reported in connection with natural sea ice in polar regions (21).

Further investigation of the concentration differences from point to point in the ice layers might produce significant results.

SECTION VII

TESTS ON LIME-TREATED ACID MINE WATER

Several partial freezing experiments were done in which the starting material was acid mine water which had been treated with lime and had a neglible iron content. Such water is produced as effluent from the currently most common type of plant for treating acid mine water. The mineral content of such water is regularly high enough so that further treatment to reduce hardness, calcium, magnesium, manganese, and sulfate is desirable. Iron and aluminum are not present in appreciable amounts in such water. Its pH is about 6.

The partial freezing procedure used for these experiments was closely similar to that used for the raw acid mine water with the bayonet-type heat exchanger.

The results of the experiments are summarized in Table VIII, which also gives most of the experimental conditions. There was good reduction of calcium, magnesium and manganese, and consequent good reduction of hardness. pH changed but little as the result of partial freezing, but the analytical results for sulfate were erratic and corresponded to poor percentage reduction of this component, if the analytical results are taken as valid.

Poor sulfate reduction was also indicated by the analytical results of experiments in which a synthetic water containing only sodium sulfate and hydrochloric acid was subjected to partial freezing. The initial pH was 4.5 and the product water pH was 6.0 in these experiments. See data on experiments 809-21 and 809-22 in Table I.

The apparent poor reduction of sulfate from these low-iron waters is not understood at this time. Sulfate reduction from all the raw Tyler Run acid mine water samples was excellent, and the same was true of a synthetic water containing only ferrous ammonium sulfate with iron in about the same concentration as in the Tyler Run waters (see 809-23 and 809-24 in Table I). The pH of the original acid mine waters as sampled was about 3 to 4 and the product waters usually had pH of about 6.

These pH values are mentioned because Malo and Baker (8) reported that pH had an effect on reduction of metal ions by partial freezing. They state that a low pH produced best reduction of alkaline earth ion concentration, while a high pH was required for good reduction of heavy metal ions. They make no reference to the effect of pH on anion reduction, nor do they give an explanation or mechanism for their observations.

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TABLE VIII

Effect of Partial Freezing on Lime-Treated Acid Mine Water

Number of Experiment	809-67	809-68	809-69	Average
Date Water Obtained, 1969	6/10	6/10	6/10	-
Date Experiment Done, 1969	6/11	6/12	6/13	-
Days Until Experiment Done	1	2	3	-
% Conversion to Ice	10	18	13	14
% Reduction Total Iron	(a)	(a)	(a)	-
% Reduction SO_4	0	26	10	-
% Reduction Hardness	96	96	96	96
% Reduction All Components (b)	89	88	89	89
pH Last Portion of Ice to Melt / pH Acid Mine Water Used	6.2 / 6.4	6.0 / 6.0	6.2 / 5.9	6.1 / 6.1
Filtered (F) or Not Filtered (U)	U	U	U	-
Nitrogen Bubbling to Stir, +	+	+	+	
Auger Stirrer with Turbine Blade, +	+	+	+	
Variac Setting	70	70	70	
Temperature of Coolant, °C	-8	-9	-8	
Duration of Cooling, minutes	54	64	60	
Freezing Rate, ml/min	7.2	11.7	8.8	
Stir-Freeze Index (c)	4.0	3.5	4.0	

(a) Iron was below 0.4 ppm and aluminum below 3 ppm in all samples.

(b) Numerical average of percent reduction of Mn, Mg, Ca, and hardness. Excludes sulfate (see text) and Fe and Al (see a).

(c) See Table III and text under Effect of Rate of Agitation.

It is tentatively concluded that the data indicating poor sulfate reduction, observed in the experiments with the lime-treated acid mine water, are the result of an interference of some kind that causes erroneous values in the colorimetric analysis for sulfate. Efforts to confirm or elucidate this were not successful.

SECTION VIII

ACKNOWLEDGEMENTS

Acknowledgement is made of the assistance of Dr. Harold L. Lovell, of the Pennsylvania State University, in providing background information on acid mine water in general, and in directing us to specific sources of such water. The suggestions of Ronald D. Hill, of the Federal Water Quality Administration, and of Dr. David R. Maneval, of the Pennsylvania Department of Mines and Mineral Industries, are also gratefully acknowledged.

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SECTION IX

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APPENDIX I

OTHER PARTIAL FREEZING EXPERIMENTS

The following four procedures are described only briefly, since they were not successful to the extent they were tried.

DIRECT FREEZING BY VAPORIZATION OF LIQUID "FREON"

Liquid "Freon 12" (dichlorodifluoromethane, CCl_2F_2) was bubbled directly through a 1/64-inch nozzle into acid mine water. When "Freon" was supplied at and expanded from a pressure of 40 psi, there was excessive local supercooling at the nozzle outlet, and ice formed as a cone-shaped solid block. This gradually grew and restricted the further flow of "Freon" so that satisfactory flow and control could not be achieved. When the pressure of "Freon" outflow was reduced to 20 psi, a mush of ice and foamy hydrate appeared and the yield of product water was negligible. This apparatus is shown in Figure 6. After the desired degree of partial freezing was reached, the refrigerant flow was stopped, the mother liquor was separated by careful decantation, and the ice allowed to melt in the original freezing vessel. Poor reduction of impurities occurred. In general, the freezing rate was rapid.

Some results are shown in Table IX and Appendix II, Experiments 809-7A, 7B.

This type of experiment was abandoned because of the excessive time consumed by operating difficulties. The original intent was to do most of the experiments by this method because all partial freezing desalting processes investigated so far have used this method, but specifically with hydrocarbons or vaporization of part of the water itself as the refrigerating source. This type of process has distinct economic advantages because no investment in a heat exchanger is necessary, and elimination of the heat exchanger reduces the resistance to heat flow between the solution being cooled and the refrigerant. This in turn reduces the temperature differences in the refrigeration unit and lowers its operating costs.

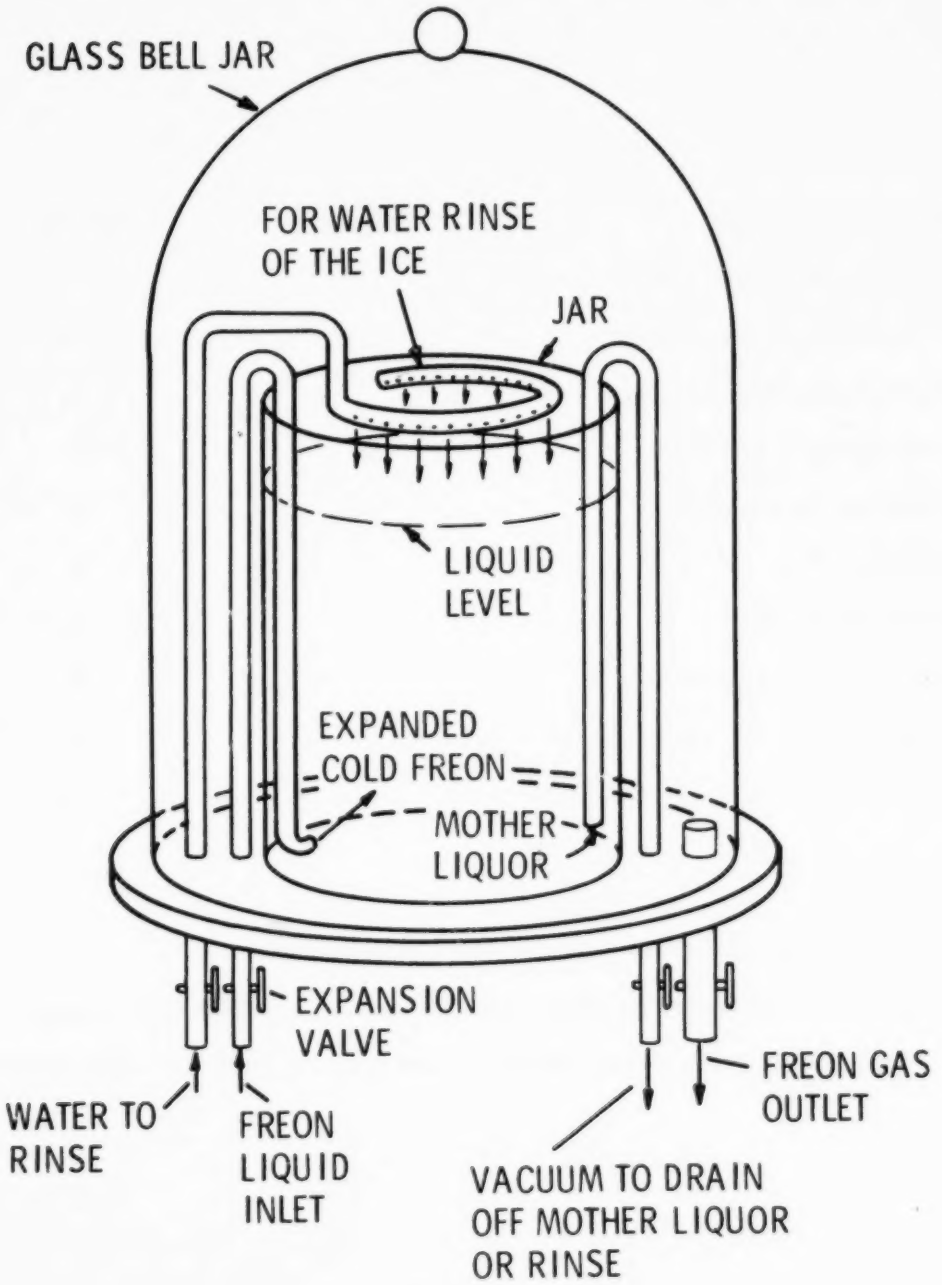

FIG. 6 A SCHEMATIC VIEW OF THE APPARATUS FOR DIRECT FREEZING

TABLE IX

Direct Freezing by Vaporization of Liquid "Freon"

Number of Experiment	809-7A	809-7B
Date Water Obtained, 1969	2/3	2/3
Date Experiment Done, 1969	2/6	2/6
Days Until Experiment Done	3	3
% Conversion to Ice (a)	58	50
% Reduction Total Iron	0	8
% Reduction SO_4	0	0
% Reduction Acidity	2	0
% Reduction All Components (b)	1	3
Filtered (F) or Not Filtered (U)	U	U
Nature of Stirring	(c)	(c)

(a) The ice was mushy and hydrate-like in appearance.

(b) Extent of analysis included only total iron, sulfate and acidity.

(c) Liquid "Freon" at 20 psi pressure was bubbled directly into lower part of container.

INDIRECT FREEZING BY VAPORIZATION OF "FREON" IN A COPPER COIL

A four-liter quantity of unfiltered acid mine water was placed in a glass jar about six inches in diameter and twelve inches high. A copper coil heat exchanger and a variable speed stirrer were then immersed in the mine water. Liquid "Freon 12" was fed into this coil through an expansion valve and the cold vapor formed passed through the copper coil. This kept it cool so that ice formed on the outer surfaces and continued to grow in thickness. After the desired ice growth was obtained, the coolant flow was stopped and the mother liquor and ice were separated and handled similarly to the procedure in the main section.

The results are given in Appendix II, Experiments 809-8A, 9A, 9B.

The poor reduction in impurities was ascribed to relatively fast cooling and inadequate agitation. For this reason, the main bulk of the experiments was done in the bayonet heat exchanger with circulating liquid refrigerant from a refrigerator unit.

DIRECT FREEZING BY ADDITION OF POWDERED DRY ICE

As explained in the Introduction under Factors Affecting Success, there is an inherent limitation to complete purification by freezing and therefore to the productive capacity of a given piece of partial freezing equipment. This affects the cost of purification. The limitation of the freezing process occurs because dissolved impurities collect and increase in concentration at the interface where ice is forming, and their removal from this interface region is limited by rates of diffusion and mixing. When concentrations of impurities become too high at the interface, these impurities become incorporated within the ice crystals.

A few experiments were done in which the refrigerant was powdered dry ice. The latter was simply sprinkled into an agitated vessel containing four literes of acid mine water, until about half of this was converted to ice crystals. The general purpose was to change the direction of the heat and mass flows during partial freezing, in the hope of achieving a basic improvement. It was hoped that superior reduction in impurities in less time would be achieved for the following reasons.

In partial freezing with indirect refrigeration, the heat flow in the water being cooled and frozen is toward the wall of the cold tube through which the coolant or refrigerant flows. The mass flow by diffusion and mixing is in the opposite direction and in most actual freezing units, the distances of flow are relatively great and the interface area is limited.

In experiments with direct refrigeration, and to an exaggerated extent with powdered dry ice, the formation of cold gaseous and dissolved gas tends to lower the heat flow toward the refrigerant (the individual particles of solid dry ice) and more important, lowering of the concentration of impurities near the interface should be aided by the flow of gaseous and dissolved carbon dioxide away from the interface of ice formation. In addition, the distances for diffusion tend to be shortened by the multiplicity of sources of cold, i.e., the individual particles of dry ice.

The results of the experiments are given in Appendix II, Experiments 147-29-1, 2.

OUTDOOR FREEZING

A considerable part of the geographical area in which acid mine water pollution exists has several months per year of cold weather during which temperatures are appreciably below freezing most of the time. It is conceivable that very low-cost outdoor natural freezing purification processes could be devised and used under such conditions, since both capital investment and operating costs would be minimized through use of open ponds for containers and natural cooling for freezing. A low rate of freezing would be expected to favor a high percentage reduction of impurities in the natural ice.

Glass jars of about 5-liter capacity, each containing 2 liters of unfiltered acid mine water were allowed to stand outdoors in temperatures of 10 to 25°F. Ice began to form on the surface after several hours' standing. Thereafter, at fifteen minute intervals, the ice formed at the surface was removed into a clean jar and the contents of the bottle were stirred vigorously for one minute. This was continued until an appreciable conversion to ice had occurred. The few outdoor freezing tests that were done indicated that the percentage reduction of impurities was not adequate to justify further interest.

The results are given in Appendix II, Experiments 147-29-3, 4, 5.

Appendix II

Analytical Data Arranged by Experiment Number

Analytical Results in Parts per Million

Experiment Number		Total Fe	Acidity	Ferrous Fe	Volume in ml
147-29-1	Direct Freezing by Dry Ice (Appendix I)				
	Starting Material	1040	2403	820	2000
	Mother Liquor	1285	2340		690
	Melt	460	832		1175
	Rinse	760	1440		540
147-29-2	Direct Freezing by Dry Ice (Appendix I)				
	Starting Material	1040	2403		2000
	Mother Liquor	930	1755		1500
	First Melt	1060	2565		120
	Second Melt	405	-		710
	Rinse	470	297		460
147-29-3	Outdoor Freezing (Appendix I)				
	Starting Material	900	1539		2000
	Mother Liquor	1120	1998		1200
	First Melt	275	630		110
	Second Melt	550	1062		230
	Third Melt	230	333		380
	Rinse				440
147-29-4	Outdoor Freezing (Appendix I)				
	Starting Material	900	1539		2000
	Mother Liquor	1040	2061		1140
	First Melt	140	575		100
	Second Melt	535	1638		155
	Third Melt	340	1215		270
	Fourth Melt	115	271		200
	Rinse	290	954		500
147-29-5	Outdoor Freezing (Appendix I)				
	Starting Material	900	1539		2000
	Mother Liquor	1250	3537		960
	First Melt	118	<100		180
	Second Melt	520	1248		310
	Third Melt	360	716		480
	Rinse	580	1063		390

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Appendix II
(cont.)

Analytical Data Arranged by Experiment Number

Analytical Results in Parts per Million

Experiment Number	Total Fe	SO_4	Acidity	Volume in ml
809-7A Direct Freezing by Expansion of Liquid Freon (Appendix I)				
Starting Material	880	2750	2120	2000
Mother Liquor	860	3000	2277	800
First Melt	950	2750	2227	380
Second Melt	820	2500	2029	400
Third Melt	900	2900	1980	380
809-7B Direct Freezing by Expansion of Liquid Freon (Appendix I)				
Starting Material	880	2750	2120	2000
Mother Liquor	810	3000	2194	900
First Melt	810	3750	2013	400
Second Melt	810	2500	2372	400
Third Melt	810	3250	2029	200
809-8A Indirect Freezing by Freon Expansion in Copper Coil (Appendix I)				
Starting Material	840	2750	2120	3000
Mother Liquor	797	2624	2492	1700
Ice Melt	890	2999	1947	1300
809-9A Indirect Freezing by Freon Expansion in Copper Coil (Appendix I)				
Starting Material	745		1946	3000
Mother Liquor	900		2293	1700
Ice Melt	530		1452	1250
Rinse	175		214	500
809-9B Indirect Freezing by Freon Expansion in Copper Coil (Appendix I)				
Starting Material	745		1946	3000
Mother Liquor	880		2227	2400
Ice Melt	615		1600	600
Rinse	145		247	500

Appendix II
(cont.)
Analytical Data Arranged by Experiment Number

Analytical Results in Parts per Million

Experiment Number	Total Fe	Acidity	Volume in ml
809-11 Indirect Freezing with Bayonet-Type Heat Exchanger			
Starting Material	400	1118	4000
Mother Liquor	390	1060	1950
First Melt	390	1019	} 2050
Second Melt	96	198	
809-12 Indirect Freezing - Bayonet Exchanger			
Starting Material	400	1118	4000
Mother Liquor	622	1772	3570
Ice Melt	294	784	430
809-13 Indirect Freezing - Bayonet Exchanger			
Starting Material	880	2674	4000
Mother Liquor	975	2612	3560
Ice Melt	344	969	440
809-14 Indirect Freezing - Bayonet Exchanger			
Starting Material	880	2674	4000
Mother Liquor	945	2828	3400
Ice Melt	404	1148	600
809-15 Indirect Freezing - Bayonet Exchanger			
Starting Material	880	2674	4000
Mother Liquor	800	3031	2100
Ice Melt	712	1729	1900
809-16 Indirect Freezing - Bayonet Exchanger - Supercooling with Flash Freeze			
Starting Material	1080	2700	4000
Mother Liquor	1035	2828	3500
First Melt	975	2700	250
Second Melt	540	1729	250
809-17 Indirect Freezing - Bayonet Exchanger			
Starting Material	1020	2816	4000
Mother Liquor	1205	3400	3100
Ice Melt	350	930	500
Rinse	30	18	2700

Appendix II
(cont.)

Analytical Data Arranged by Experiment Number

Analytical Results in Parts per Million

Experiment Number	Total Fe	Al	Mn	Mg	Ca	SO_4	Acidity	Volume in ml	pH
809-18 Indirect Freezing - Bayonet Exchanger									
Starting Material	800	110	10	212	126	1660		4000	4.0
Mother Liquor	800	124	11	212	160	2320		3110	3.5
First Melt	640	100	11	72	112	2110		412	4.0
Second Melt	164	40	4	28	34	520		420	4.5
Rinse (tap water)	160	<3	<1	16	44	140		3000	7.5
809-19 Indirect Freezing - Bayonet Exchanger									
Starting Material	720	120	11	108	138	1500		4000	3.5
Mother Liquor	800	124	12	116	148	2560		3115	4.0
Ice Melt	440	90	8	64	88	580		755	4.5
Rinse	32	<3	<1	22	44	26		3500	6.5
809-20 Indirect Freezing - Bayonet Exchanger									
Starting Material	760	130	11	108	144	3480		4000	4.0
Mother Liquor	1080	170	16	164	200	4440		1675	3.5
First Melt	1200	170	12	164	154	5000		505	4.5
Second Melt	520	80	7	104	96	1400		670	4.5
Third Melt	216	35	3	60	46	680		935	5.0
Rinse	60	<3	<1	9	14	240		3000	
809-21 Indirect Freezing - Bayonet Exchanger - Synthetic Water, Na_2SO_4, HCl									
Starting Material						1700		4000	4.5
Mother Liquor						3100		3120	5.0
First Melt						2250		110	5.0
Second Melt						1600		330	5.5
Third Melt						1400		380	6.0
Rinse						300		2300	6.0
809-22 Indirect Freezing - Bayonet Exchanger - Synthetic Water, Na_2SO_4, HCl									
Starting Material						5600		4000	4.5
Mother Liquor						5600		2450	4.0
First Melt						5500		180	4.5
Second Melt						4600		120	5.0
Third Melt						1500		1250	6.0
Rinse						400		2800	6.0

Appendix II
(cont.)

Analytical Data Arranged by Experiment Number

Analytical Results in Parts per Million

Experiment Number	Total Fe	Al	Mn	Mg	Ca	SO_4	Acidity	Fe^{++}	Volume in ml	pH	Ratio Fe^{+} /Total Fe
809-23 Indirect Freezing - Bayonet Exchanger - Synthetic Water, Fe $(NH_4SO_4)_2$											
Starting Material	940					2750		916	4000	2.5	97
Mother Liquor	1300					3500		1230	2450	2.0	95
First Melt	1060					2500		984	80	3.5	93
Second Melt	853					2000		812	190	3.5	96
Third Melt	267					700		180	1100	5.0	67
Rinse	15					40		12	3000	5.5	77
809-24 Indirect Freezing - Bayonet Exchanger - Synthetic Water, Fe $(NH_4SO_4)_2$											
Starting Material	872					4800		836	4000	3.0	96
Mother Liquor	1288					6500		1264	2750	2.0	98
First Melt	556					3800		552	55	4.0	100
Second Melt	572					4100		536	125	4.0	94
Third Melt	160					2600		120	1050	5.0	75
Rinse	6					10		6	2950	6.0	100
809-25 Indirect Freezing - Bayonet Exchanger											
Starting Material	856	120	12	32	32		2324	728	3900	4.0	85
Mother Liquor	1024	140	16	54	36		2753	952	2550	4.0	93
First Melt	912	140	8	53	32		2418	832	165	4.5	91
Second Melt	572	80	6	45	28		1537	536	145	4.5	94
Third Melt	256	40	2	4	14		538	208	900	5.0	81
809-27 Indirect Freezing - Bayonet Exchanger											
Starting Material	816	110	12	72	46		2230	700	4000	4.0	86
Mother Liquor	1040	140	16	72	66		3089	968	2750	4.0	93
First Melt	712	100	12	40	40		1763	624	102	4.0	88
Second Melt	720	80	6	24	28		1279	424	166	4.0	59
Third Melt	160	20	2	4	8		359	120	1000	5.0	75
809-29 Indirect Freezing - Bayonet Exchanger											
Starting Material	784	110	12	56	60		2231	728	4000	4.0	93
Mother Liquor	1032	150	16	88	76		3035	960	2600	4.0	93
First Melt	960	140	12	72	64		2543	856	120	4.0	89
Second Melt	536	70	6	40	44		1482	456	166	4.5	85
Third Melt	288	60	2	33	16		592	208	1200	5.0	72
809-32 Indirect Freezing - Bayonet Exchanger											
Starting Material	692	108	9	212	60	1920	1920	646	4000	4.0	93
Mother Liquor	936	130	11	104	70	2260	2880	808	3100	4.0	86
First Melt	360	51	4	24	28	800	1110	272	86	4.5	76
Second Melt	176	33	2	24	14	500	590	176	83	5.0	100
Third Melt	72	8	1	6	4	200	178	64	750	5.5	89

Appendix II
(cont.)

Analytical Data Arranged by Experiment Number
Analytical Results in Parts per Million

Experiment Number	Total Fe	Al	Mn	Mg	Ca	SO_4	Acidity	Fe^{++}	Volume in ml	pH	Ratio Fe^{++} /Total Fe
809-34 Indirect Freezing - Bayonet Exchanger											
Starting Material	216	120	16	96	56	520	2240		4000	4.0	
Mother Liquor	172	140	18	112	80	1200	2570		3175	4.0	
Ice	76	15	2	12	8	200	257		825	5.0	
809-38 Indirect Freezing - Bayonet Exchanger											
Starting Material	656	106	9	92	54	1550	2240	532	4000	3.5	81
Mother Liquor	800	124	10	104	64	1610	2700	664	3100	4.0	83
First Melt	640	108	8	72	44	1440	2080	520	100	4.0	81
Second Melt	368	63	5	44	26	370	1130	304	100	4.0	83
Third Melt	120	8	1	14	8	200	297	80	700	5.5	67
809-40 Indirect Freezing - Bayonet Exchanger											
Starting Material	424	104	9	96	56	1570	2160		4000	4.0	
Mother Liquor	496	128	12	112	72	2050	2840		2450	4.0	
First Melt	516	134	11	108	64	1940	2730		109	4.0	
Second Melt	424	110	9	84	48	1900	2140		85	4.0	
Third Melt	212	51	4	37	24	950	890		1350	4.5	
809-43 Indirect Freezing - Bayonet Exchanger											
Starting Material	640	174	8	80	29	2020	2416		4000	2.9	
Mother Liquor	824	248	10	120	36	2030	3009		2375	2.9	
First Melt	584	248	10	104	31	1900	3010		88	3.3	
Second Melt	240	80	4	32	14	890	1043		1550	3.7	
809-44 Indirect Freezing - Bayonet Exchanger											
Starting Material	576	164	8	64	27	1680	2050		4000	---	
Mother Liquor	668	200	9	96	30	1750	2420		2650	3.3	
First Melt	712	236	10	104	30	1300	2590		354	3.4	
Second Melt	224	86	4	33	17	960	840		1000	3.5	
809-47 Indirect Freezing - Bayonet Exchanger											
Starting Material	640	116	8	112	26	2560	1880		4000	3.2	
Mother Liquor	784	144	10	152	31	3340	2480		3000	3.4	
First Melt	280	60	4	64	17	1220	875		75	4.1	
Second Melt	80	40	1	40	7	360	274		100	3.9	
Third Melt	21	12	<1	4	3	130	73		950	4.3	

Appendix II
(cont.)

Analytical Data Arranged by Experiment Number

Analytical Results in Parts per Million

Experiment Number	Total Fe	Al	Mn	Mg	Ca	SO_4	Acid-ity	Volume in ml	pH
809-49 Indirect Freezing - Bayonet Exchanger									
Starting Material	608	104	8	104	28	2330	1900	4000	3.3
Mother Liquor	840	136	11	168	35	3380	2860	2650	3.4
First Melt	280	108	4	48	21	1360	1040	130	4.0
Second Melt	184	40	1	48	6	380	283	150	4.1
Third Melt	20	12	<1	4	4	120	82	1100	4.1
809-50 Indirect Freezing - Bayonet Exchanger									
Starting Material	680	90	8	104	27	2160	1940	4000	3.5
Mother Liquor	640	90	8	96	30	2600	1920	3500	3.4
First Melt	160	28	3	32	11	600	510	75	3.6
Second Melt	41	16	<1	8	5	170	165	110	3.9
Third Melt	12	12	<1	3	2	<10	73	300	4.3
809-53 Indirect Freezing - Bayonet Exchanger									
Starting Material	548	107	9	77	26	2760	2010	4000	3.0
Mother Liquor	800	161	13	104	35	3660	3160	2200	3.2
First Melt	456	90	7	66	24	1950	1780	120	3.3
Second Melt	152	29	2	25	9	560	494	225	3.4
Third Melt	72	15	1	12	6	240	275	300	3.6
Fourth Melt	21	6	<1	5	3	60	91	1050	4.4
809-54 Indirect Freezing - Bayonet Exchanger									
Starting Material	568	96	10	77	26	2760	2050	4000	3.0
Mother Liquor	832	152	14	108	36	3660	3350	2300	3.0
First Melt	464	85	8	67	22	2000	1720	140	3.0
Second Melt	100	18	2	16	10	400	330	240	3.2
Third Melt	28	8	1	6	4	140	128	175	3.4
Fourth Melt	25	6	1	5	4	120	100	120	3.5
Fifth Melt	17	4	<1	2	2	60	64	1050	3.7
809-55 Indirect Freezing - Bayonet Exchanger									
Starting Material	540	102	10	77	26	2320	2040	4000	3.1
Mother Liquor	736	146	13	110	35	3520	2920	2550	3.1
First Melt	356	60	6	49	18	1360	1190	135	3.1
Second Melt	88	18	2	16	8	340	330	300	3.4
Third Melt	17	4	<1	4	3	60	147	800	3.7

Appendix II
(cont.)

Analytical Data Arranged by Experiment Number

Analytical Results in Parts per Million

Experiment Number	Total Fe	Al	Mn	Mg	Ca	SO_4	Acidity	Volume in ml	pH
809-57 Indirect Freezing - Bayonet Exchanger									
Starting Material	580	92	9	97	47	2490	1940	4100	3.3
Mother Liquor	688	114	11	102	55	3680	2330	3150	3.5
First Melt	126	20	2	21	16	600	415	325	3.9
Second Melt	10	<3	<1	2	2	30	55	330	4.3
Third Melt	4	<3	<1	<1	1	10	28	350	4.4
809-58 Indirect Freezing - Bayonet Exchanger									
Starting Material	556	92	9	84	51	2640	1860	4000	3.4
Mother Liquor	880	140	15	120	70	4080	3060	2350	3.4
First Melt	236	52	5	52	38	1540	1060	150	3.7
Second Melt	45	14	1	9	10	200	165	200	4.1
Third Melt	30	8	<1	5	6	130	110	1320	4.3
809-59 Indirect Freezing - Bayonet Exchanger									
Starting Material	568	96	9	83	49	2340	1920	4000	3.4
Mother Liquor	620	107	10	92	51	2940	1970	3500	3.3
First Melt	132	24	2	24	18	700	420	84	3.6
Second Melt	22	4	<1	5	4	60	88	420	4.4
809-60 Indirect Freezing - Bayonet Exchanger									
Starting Material	552	96	9	86	42	2500	1860	4000	3.3
Mother Liquor	608	104	10	92	50	2800	2010	3640	3.5
First Melt	172	32	3	30	24	550	530	40	3.8
Second Melt	64	17	1	14	11	90	216	40	
Third Melt	17	<3	<1	5	4	<10	49	280	4.1
809-61 Indirect Freezing - Bayonet Exchanger									
Starting Material	568	96	9	86	49	2600	1800	4000	3.6
Mother Liquor	608	107	10	90	52	2700	1960	3650	3.5
First Melt	132	22	2	24	18	680	392	70	3.6
Second Melt	18	4	<1	3	4	90	78	300	4.1

Appendix II
(cont.)

Analytical Data Arranged by Experiment Number

Analytical Results in Parts per Million

Experiment Number	Total Fe	Al	Mn	Mg	Ca	SO_4	Total Hardness	Volume in ml	pH
809-67 Indirect Freezing - Bayonet Exchanger - Lime-Treated Acid Mine Water									
Starting Material	(c)	(c)	4	112	260	1500	2250(a)	4000	6.4
Mother Liquor	(c)	(c)	5	123	260	1450	2570(a)	3660	6.4
First Melt	(c)	(c)	1	18	78	1500	240(a)	80	5.4
Second Melt	(c)	(c)	<1	8	4	1500	43(b)	300	6.2
809-68 Indirect Freezing - Bayonet Exchanger - Lime-Treated Acid Mine Water									
Starting Material	(c)	(c)	4	116	272	1750	2245(a)	4000	6.0
Mother Liquor	(c)	(c)	5	134	280	1750	2160(a)	3300	6.1
First Melt	(c)	(c)	1	14	66	1300	130(a)	300	6.1
Second Melt	(c)	(c)	<1	5	13	1300	53(b)	400	6.0
809-69 Indirect Freezing - Bayonet Exchanger - Lime-Treated Acid Mine Water									
Starting Material	(c)	(c)	4	120	266	1400	2290(a)	4000	5.9
Mother Liquor	(c)	(c)	5	128	260	1600	2810(a)	3500	6.1
First Melt	(c)	(c)	<1	14	66	1300	180(a)	200	6.0
Second Melt	(c)	(c)	<1	6	30	1300	101(b)	100	6.2
Third Melt	(c)	(c)	<1	3	8	1200	32(b)	225	6.1

(a) Water Hardness determined by EDTA titration, expressed in ppm $CaCO_3$.

(b) Water Hardness calculated from ppm Mg and Ca, since EDTA titrations are not sensitive enough in this low concentration range.

(c) Total iron less than 0.4 ppm and Al less than 3 ppm in all samples.

APPENDIX III

Numbers refer to those used in Section on References and Notes

1. Schroeder, W. C., and Marchello, J. M. "Study and Analysis of the Application of Saline Water Processes to Acid Mine Waters." Office of Saline Water, Research and Development Progress Report No. 199. Washington, D. C., August, 1966.

This abstract deals only with Section VIII, entitled "Crystallization Processes Applied to Kittanning Run."

The report discusses three freezing processes for saline waters (direct, secondary and hydrate processes) under consideration by OSW at the time the report was written. It mentions direct freezing desalting plants abroad, with special reference to Colt process (Fairbanks-Morse) plants. It refers repeatedly to expectation of improvements that will result in cost reductions for freezing process. It cites Blaw Knox pilot plant studies with respect to the secondary process. Uses the cost and design data for the large scale plants and analogous estimates for the hydrate process to estimate costs for acid mine water plants. Gives capital costs and operating costs for all three kinds of plant. The calculated cost of water containing 400-500 ppm total dissolved solids is about 70¢/1000 gals.

It is not clear where Kittanning Run information is used in the estimates. The report assumes that freezing plants designed for salt water would give a satisfactory product when operated on acid mine water. Detailed data are supplied in a computer output supplement which was not consulted.

7. Rose, Arthur, and Sweeny, R. F. "Waste-Water Renovation, Part 2. Feasibility Tests of Freezing." Public Health Publication No. 999-WP-4. Cincinnati, Ohio, 1963.

Fourteen actual freezing tests were completed on secondary effluent from the Pennsylvania State University waste treatment plant. Eight were carried out in the 40-gpd Rose Process pilot plant with isobutane as the refrigerant (direct process). Other tests were made by direct addition of powdered dry ice. The results showed that chemical oxygen demand (COD) was reduced 65 to 85 percent; chlorides, 85 to 90 percent; and conductivity, 90 percent or more. Reduction of alkyl benzene sulfonate (ABS) was erratic. The isobutane used as a refrigerant interfered in the COD tests. With data from the better test runs, preliminary cost estimates indicate that 95 percent of the feed water containing 10 percent of the contaminants can be recovered at a cost somewhat lower than that predicted for desalinating sea water by freezing.

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8. Malo, B. A., and Baker, R. A. "Cationic Concentration by Freezing," in "Trace Inorganics in Water." Advances in Chemistry Series No. 73, American Chemical Society, Washington, D. C., 1968.

The results are reported of an investigation of cationic separation during the freezing process as it applies to concentration of trace contaminants from water. The cations, including Fe, Cu, Zn, Mn, Pb, Ni, Ca, Mg, and K, were studied at concentrations of 0.1 to 10 mg/liter. For any given cation, recovery does not vary over the experimental concentration range. However, selective ion incorporation into the ice matrix was observed when demineralized laboratory-prepared solutions and highly mineralized naturally buffered waters were concentrated. Increasing the mixing rate up to some limiting value increases cationic recovery. Whether initial pH increases or decreases, recovery depends on the nature of the cation. Alkali metals (K, Ca, and Mg) concentrate best at acid pH. Heavy metal cations (Pb, Ni, and Cu) concentrate best at alkaline pH. Generally, increasing the initial total dissolved solids decreases cationic recovery.

9. Baker, R. A. "Trace Organic Contaminant Concentration by Freezing. I. Low Inorganic Aqueous Solutions." Water Research 1, 61 (1967).

The freezing concentration of μ/liter and mg/liter concentrations of various organics (phenol, various substituted phenols, propionic through caproic volatile fatty acids and acetophenone) in aqueous solution may be quantitatively accomplished in a single stage or a cascade of single stage steps in the absence of dissolved inorganic salts.

10. Baker, R. A. "Trace Organic Contaminant Concentration by Freezing. II. Inorganic Aqueous Solutions." Water Research 1, 97 (1967).

The presence of dissolved inorganic salts in aqueous solution impairs the recovery efficiency of organic solutes by a freezing concentration procedure. When dissolved salts are present, the mixing rate, sample pH and volume concentration ratio become critical in organic solute recovery efficiency.

11. Kobayashi, S., and G. F. Lee. "Freeze Concentration of Dilute Aqueous Solutions." Anal. Chem. 36, 2197 (1964).

The authors proved the effectiveness of progressive freezing as a method of solute concentration by showing the recovery percentages of NaCl and Rhodamine B. The percent recovery for NaCl is 97 to 102.7 and for Rhodamine B is 87 to 91.

12. Smith, G. H., and Tasker, M. P. "Freeze Concentration of Dilute Solutions." Anal. Chim. Acta 33, 559 (1965).

The recovery of the following solutes from a dilute solution is 100% even at solute concentrations of less than 1 ppm: Na_2HPO_4, NaF, NaCl, $Mg(NO_3)_2$ and SiO_2(as Na_2SiO_3).

BIBLIOGRAPHIC: Applied Science Laboratories, Inc.
Purification of Acid Mine Water by Freezing. Report FWQA Grant No. 14010 DRZ, September, 1970

ACCESSION NO:

KEY WORDS:

Acid Mine Water
Freezing Purification
Ferrous Iron Reduction
Lime-Treated Acid Mine Water
Hardness Reduction
pH Change
Coal Mine Drainage

Acid mine drainage (AMD) was subjected to partial freezing to the extent of 50% conversion to ice. Percent reduction of various metal and acid components in the product water was consistently in the general neighborhood of 85 to 90%, some individual components were reduced to 98% on occasion.

Reduction of metal ions was observed in similar freezing experiments using AMD that had been treated with lime; reduction in hardness of this water was

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